

Structure and Properties of Electrodeposited Ag-Sn Alloys

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Electrodeposited (ECD) silver-tin alloys are attractive materials for both decorative finishing and engineering applications. Silver displays low tarnishing resistance under exposure to sulphide containing environments, also in ordinary atmospheric conditions (1), in the presence of small quantities of hydrogen sulphide or carbonyl sulphide (2). This is a point of major concern when pure silver is used for electronic applications, where contact reliability and solderability are mandatory, and, of course, for silverware, jewellery and the like, because of the loss of aesthetic appeal of the metal. Moreover, sulphide films on silver do not exert any protective function upon the underlying metal and their growth can be very fast: a silver sheet, 1mm thick, is completely sulphidised in only 1 minute at 400°C (3). Silver tarnishing resistance can be significantly increased through alloying, without prejudice of valuable properties such as low contact resistance, good solderability and attractive appearance. In particular, silver-tin alloys show substantially higher tarnish resistance than pure silver (4). Furthermore, while silver shows rather poor mechanical properties, which makes it unsuitable for applications where hardness and wear-resistance are required, its alloys are by no means superior in this respect.

Since the work of Leidheiser and Ghulam (5), there has been only a scanty interest about silver-tin alloys plating, mostly due to the difficulty in mastering solution chemistry, apart from the copybook case of alkaline bath containing cyanide. The large potential gap between Ag and Sn (0.8 and -0.136 V NHE, respectively) calls for the use of a strong and stable complexant, such as cyanide, thiocyanate or thiosulphate. The use of anionic ligands sets a limit to the practical pH range of the solution, forcing to choose alkaline electrolytes containing tin as stannate. In fact, silver-tin electrodeposition, apart from Sn-Ag solder alloy, has been successfully reported almost invariably from alkaline baths, such as silver cyanide-tin pyrophosphate (6-8) or silver iodide and tin pyrophosphate baths (9). Exceptions to this rule, turning to elaborate electrolyte compositions, can be found in the patents literature (see, for example, 10).

In order to develop an acidic bath for plating Ag-Sn alloys in the composition range 10÷25%at Sn, a solution containing thiourea as silver ligand was chosen. Thiourea forms cationic complexes with a number of transition metal ions, particularly with those of the IB group elements. Gold and silver complexes are among the most stable thiourea complexes. They have been the subject of intensive research, due to the possible application in precious metals extraction and recovery (11, 12), metal cleaning and electropolishing (13). Two different bath compositions were studied, both containing thiourea: a simple methansulphonate acid bath, based on a commercially available tin plating solution, which turned out to be rather unstable; and a thiourea-silver sulphate solution with addition of tin sulphate in low concentration

and stabilisers for tin and silver, which showed good chemical stability and reproducibility of deposit composition. On this basis, deposition conditions were defined and a detailed study of deposits structure and properties was carried out. Ag-Sn deposits were obtained from solutions containing $[Ag^+]$ 0.1÷0.2M and $[Sn^{2+}]$ up to 0.06M, at cd 4÷10 mA/cm², room temperature and without stirring. Deposits were analysed by X-ray diffraction, atomic force microscopy and scanning electron microscopy. Mechanical properties and tarnishing resistance of the coatings were also assessed.

ECD Ag-Sn alloys, in the composition range 13.5÷23.5at.%Sn, shows the hexagonal close packed structure, similar to the metallurgical ζ phase. The composition range corresponding to the intermetallic compound Ag₃Sn (ϵ -phase, with orthorhombic lattice) appears to be forbidden to electrodeposition: for Sn content higher than about 23.5at, biphasic ζ + β Sn alloy films are obtained, in condition of morphological instability, and final formation of powdery deposits. The relationship between phase structure and electronic concentration (ratio of valency electrons to the number of atoms, e/a) has been investigated, obtaining a correlation between the axial ratio c/a for hcp alloys and e/a , in agreement with the findings of King and Massalski for the ζ phases of the metallurgical system Ag-Sn (14). The ECD ζ phase Ag_xSn shows either [10.1] or [00.1] preferred orientation, with matte and bright appearance respectively, depending on tin content. Ag-Sn20%at films were tested as anti-tarnishing finish on ECD silver, according to ISO 4538:1998, showing that the Ag-Sn top layer can be a valuable protection at thickness as low as 0.3 μ m. Mechanical properties were derived from the indentation load – displacement behaviour of Ag_xSn coatings: at 0.5N load, thick coatings showed microhardness value of 260HV and elastic modulus in the range of 85 GPa.

References

- ¹ A. Butts, *SILVER Economics, Metallurgy, and Use*, Robert E. Krieger Publishing Company, Malabar, Florida (1982).
- ² T.E. Graedel, J.P. Franey, G. J. Gualtieri, G.W. Kammlott and D.L. Malm, *Corros. Sci.*, **25**, 1163 (1985).
- ³ S. Mrowec and K. Przybylski, *Oxidation of Metals*, **23**(3/4), 107 (1985).
- ⁴ M. Jordan, *The Electrodeposition of Tin and its Alloys*, Eugen G. Leuze Publishers, Saulgau/Württ, German (1993).
- ⁵ H. Leidheiser, Jr. and A. R. P. Ghuman, *J. Electrochem. Soc.*, **120**, 484 (1973).
- ⁶ N. Kubota and E. Sato, *Electrochim. Acta*, **29** (1984) 361.
- ⁷ N. Kubota and E. Sato, *Electrochim. Acta*, **30** (1985) 305.
- ⁸ J. Cl. Puipe and W. Fluehmann, *Plat. & Sur. Finish.*, January '83 (1983) 46.
- ⁹ S. Arai and T. Watanabe, *Materials-Transactions-JIM.*, **39**(4), 439 (1998); *J. Japan Inst. Met.*, **60**(12) 1149 (1996).
- ¹⁰ G. Herklotz, T. Frey, W. Hempel, *Electroplating bath for the electrodeposition of silver-tin alloys*, US Patent US5514261 (1996).
- ¹¹ J. B. Hiskey, *Gold and Silver: Leaching, Recovering and Economics*, W. C. Larson and J. B. Hiskey eds., SME – AIME Littleton, CO (1981); p. 83.
- ¹² T. Groenewald, *J. Appl. Electrochem.*, **5**, 71(1975).
- ¹³ G. I. Edson, *Precious Metals 1990*, International Precious Metals Institute, USA (1990); p. 251.
- ¹⁴ H. W. King and T. B. Massalski, *Phil. Mag.*, **6**, 669 (1961).